Renewable and Sustainable Energy Reviews 32 (2014) 936–943

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Recovery of solar grade silicon from kerf loss slurry waste

Nadjib Drouiche [a,*], Patricia Cuellar [b], Fouad Kerkar [a], Sidali Medjahed [a], Nabila Boutouchent-Guerfi [a], Malek Ould Hamou [c]

[a] Centre de Recherche en technologie des Semi-conducteurs pour l'Energétique (CRTSE). 2, Bd Frantz Fanon BP140, Alger–7 merveilles 16027, Algeria
[b] Process Engineer Water Treatment, ManEngenius, The Netherlands
[c] Laboratoire Pédagogique du Génie Minier, Département de Génie Minier de l'Ecole Nationale Polytechnique (ENP), Alger, Algeria

ARTICLE INFO

Article history:
Received 7 November 2013
Received in revised form
9 January 2014
Accepted 27 January 2014
Available online 14 February 2014

Keywords:
Kerf loss
Silicon carbide
Silicon recovery
Photovoltaic
Electric field
Centrifugation

ABSTRACT

During the last two decades and, particularly, in recent years, the photovoltaic sector has increased interest in the recovery of solar grade silicon (SOG). In order to further develop related technologies and to find suitable commercial applications for its recovery, it is essential to understand the current scientific know-how and advances. This review paper copes with recently published scientific articles in which the recovery of solar grade silicon has been studied. In addition, the present work provides an updated picture of the current understanding of the theory behind the employed technologies. The techniques discussed were divided into six categories, which are: (i) alloying process, (ii) hydrobromination, (iii) supercritical water, (iv) electrophoresis and gravitational settling, (v) directional solidification, and (vi) centrifugation.

Contents

1. Introduction

In the past few years, the availability of polysilicon feedstock has been a critical issue for the rapidly growing PV industry. The tight supply situation has caused very high polysilicon spot market prices (up to 260 €/kg in 2008) and has limited production expansion by the industry.

* Correspondence to: Centre de Recherche en technologie des Semi-conducteurs pour l'Energétique (CRTSE). 2, Bd Frantz Fanon BP140, Alger – 7 merveilles, 16027, Algeria. Tel.: +213 21 279880x192; fax: +213 21 433511.
E-mail addresses: nadjibdrouiche@yahoo.fr, droui2@unesco-ihe.org (N. Drouiche).

http://dx.doi.org/10.1016/j.rser.2014.01.059
1364-0321

On the other hand, polysilicon has triggered a rapid innovation in wafer production and cell manufacturing lowering the silicon consumption per W of module power produced. Silicon usage is currently 7 g/W, whereas it was typically 10 g/W for the year 2007. As an important fact, the reduction of silicon is of high priority, nevertheless, since the feedstock price has now been reduced, the pressure to reduce silicon usage has lately diminished.

Crystalline silicon modules are manufactured in six steps: (i) silicon production, (ii) silicon purification, (iii) silicon crystal growth, (iv) ingot slicing, (v) cell fabrication and, (vi) device processing for encapsulation. Given that, the cost distribution is dominated by the silicon wafer manufacturing, the solar silicon grade recovery is seen as an important parameter in low-cost manufacturing (Fig. 1).

Solar grade silicon (polysilicon) is the basic ingredient of crystalline silicon modules. It is melted and solidified using a variety of techniques to produce ingots with different degrees of crystal perfection. The most relevant crystallization technology is directional solidification. It is based on either single-crystal silicon grown by the Czochralski (Cz) method (2010: 33% of the market) or polycrystalline silicon by casting (2010: 53% of the market) [1].

The ingots formed by both methods are sliced into thin wafers by wire sawing. Wafers are processed into solar cells and interconnected in weatherproof packages designed to last for at least 25 years. A layer of silicon of about 250 μm thick is lost per wafer, representing more than 30 wt% of the silicon value.

The kerf loss goes into slurry waste during the processing and it is compounded by silicon, silicon carbide, metal fragments and mineral-oil-based or glycol-based slurry vehicle. It can be considered as a new source of production of low-cost solar-grade polysilicon feedstock material with the potential to recover enough polysilicon to generate over 300 MW/year of crystalline silicon solar cells, i.e., more than two times the size of the current silicon solar-cell production.

Recently, silicon recovery from the kerf loss slurry waste has attracted incessant attention on the separation of the components due to the high purity silicon material. Several purification methods have been developed for the removal of SiC such as: alloying process [2], hydrobromination [3,4], supercritical water [5], electrophoresis and gravitational settling [6,7], Phase-transfer separation method [8], and centrifugation [9–11].

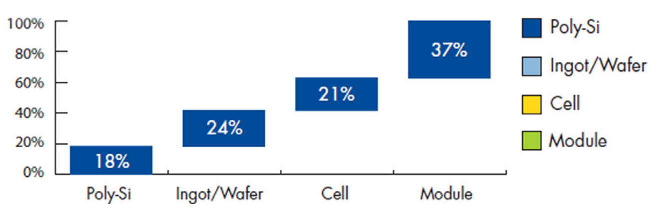


Fig. 1. Relative cost distribution of the production of crystalline silicon PV module.

This work aimed to review studies conducted mainly during 2008–2013, covering a wide and versatile range of feasible techniques applied in the recycling of silicon cutting kerf loss.

2. Background

2.1. Semiconductor grade silicon production

The silicon PV industry has been relying on waste materials from the semiconductor Si industry regarding the feedstock material used in crystal growth. The waste material needed by the PV industry amounts to about 10% of the polysilicon material used by the semiconductor Si industry.

Semiconductor-grade polysilicon is mostly produced by the trichlorosilane ($SiHCl_3$) distillation and reduction method (Fig. 2) [12,13]. The trichlorosilane is manufactured by fluidizing a bed of fine pulverized metallurgical-grade silicon (MG-Si) with hydrogen chloride in the presence of a copper-containing catalyst. The MG-Si, is produced by the reduction of natural quartzite (silica) with coke (carbon) in an electric arc furnace. It can be noticed that the semiconductor-grade polysilicon material produced by this method far exceeds the purity requirement of the PV industry [14,15].

The main reactions that take place during the semiconductor Grade Silicon (SGS) production steps are:

1. Production of metallurgical grade silicon (MGS) by heating silica with carbon.

   $C\ (s) + SiO_2\ (s) \rightarrow Si\ (l) + SiO\ (g) + CO\ (g)$

2. Purification of MG silicon through a chemical reaction to produce a silicon-bearing gas of trichlorosilane ($SiHCl_3$).

   $Si\ (s) + 3HCl\ (g) \rightarrow SiHCl_3\ (g) + H_2\ (g) + heat$

3. Reaction of $SiHCl_3$ and hydrogen in a process called Siemens to obtain pure semiconductor-grade silicon (SGS).

   $SiHCl3\ (g) + 2H_2\ (g) \rightarrow 2Si\ (s) + 6HCl\ (g)$

2.2. Principles of wafer slicing

Wafer slicing, also called “wafering”, is a key part of the solar photovoltaic (PV) cell manufacturing process. The wafering process begins with solid ingots made of single-crystal or multi-crystalline

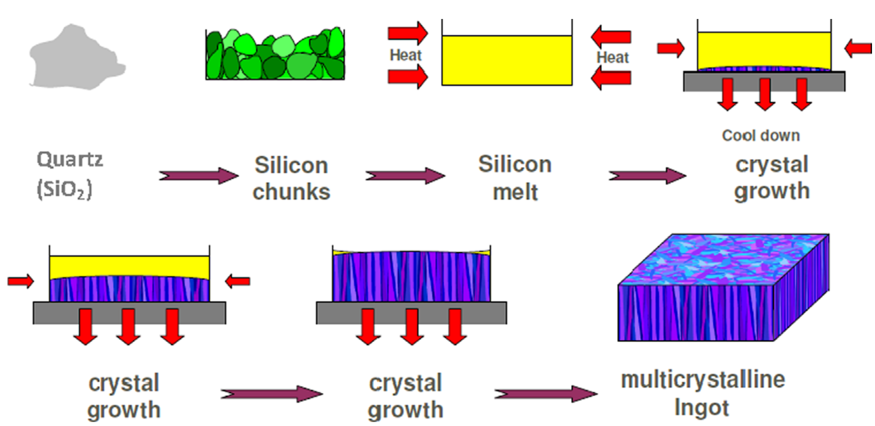


Fig. 2. Multicrystalline ingot manufacturing steps.

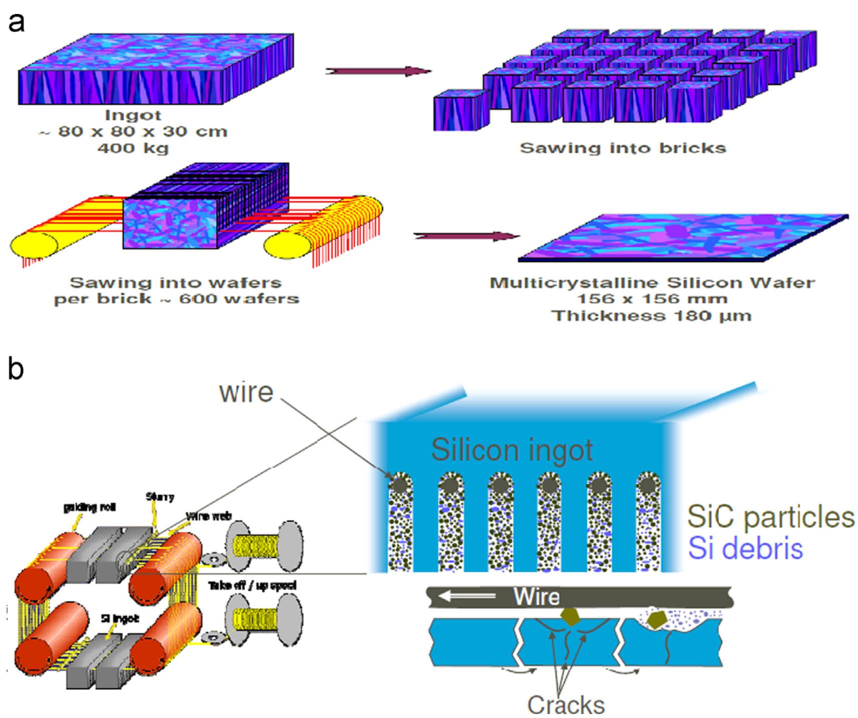


Fig. 3. Wafers manufacturing steps.

silicon material. Wire saws shape the ingots into squared blocks which dimensions are about 150 cm × 150 cm × 60 cm (Fig. 3). The large casting normally weighs 240 kg before it is sawed into bricks. Later, the bricks are sliced into thin wafers which are used as the base for the active PV cell. Wire sawing is nowadays largely – if not exclusively – achieved by means of Multi-Wire Saw technology (MWS) [16–18] which was introduced in the mid 1980s as a PV wafering tool. This machine is equipped with wire having several hundred kilometers long. The wire is arranged in such a way that the ingot is sliced into hundreds of wafers simultaneously. The process takes around six hours at a speed of up to 60 km/h, the resultant slices are approximately 180 μm thick. An abrasive like silicon carbide or diamond is added to oil or Polyethylene Glycol (PEG) to make abrasive slurry. This slurry is sprayed on the wire as it moves through the material being sliced. During the slicing operation, moving wire carrying abrasive slurry to create the cutting action is used so a thin layer of cutting slurry is deposited onto the wire [19,20].

The densities of the carrier fluid can vary from approximately 0.85 kg/l for oil-based fluids to over 1.12 kg/l for polyethylene glycol (PEG). In order to create an effective cutting fluid [24], various ratios of the abrasive powder are used for the suspending liquid. One common mixture is 48 wt% of silicon carbide combined with 52 wt% polyethylene glycol. The resulting slurry has a combined density of 1.634 kg/l [21].

The wire serves only as the transport mechanism. The combination of wire diameter, nominal abrasive size, carrier vehicle viscosity, and abrasive shape determine the kerf loss of the cutting process [22,23].

2.3. Evaluation principles

Slicing is the first major post crystal growth manufacturing process towards wafer production. Solar grade silicon wastes produced during the slicing of multi-crystalline silicon ingots, and used for photovoltaic (PV) solar cells production, contains wastes from the sawing slurry. Huge quantity of the silicon feedstock is lost in the mixture which is mainly composed from silicon carbide, metal fragments, glycol and silicon.

The amount of silicon waste formed during the slicing step depends on the diameter of the cutting steel wire. Nowadays, the wafer thickness is approaching a wire diameter of 150–180 μm. As a result, the exhausted slurries contain up to 10% of silicon. Therefore, recycling cutting slurry from the slicing process is a very important alternative that should be considered due to the economic value that it represents.

The separation of silicon (Si) and silicon carbide (SiC) from slurry waste is a hard task because of they own similar properties.

3. Overview of different techniques recently used for si recycling

The following Sections (from Sections 3.1 to 3.6) in this Chapter report a summary of recent investigations with regard to the separation of Si/SiC describing different types of processes which are divided into categories according to each topic.

3.1. Electrical field

Hazardous sawing waste containing very small Si particles is produced from the silicon wafer manufacturing for solar cells causing serious environmental pollution problems. Consequently, the recycling of Si and abrasives from this waste is considered an effective option to minimize its environmental impact.

The separation of Si/SiC and Si/Al_2O_3 mixtures applying electrophoresis and gravitational settling has previously been reported [6]. The experiment consisted in analyzing the separation performance of Si and Al_2O_3 at pH 2.5 and pH 9 (IEP for Si and Al_2O_3, respectively) using a separation cell of 15 cm depth and 15 cm long. Under a pH value of 9 the separation performance was better than at pH 2.5. In contrast, the separation performance between Si and SiC was lower than that achieved for Si and Al_2O_3. The Al_2O_3 contents remaining in the Si/Al_2O_3 mixture were 9 wt% (minimum value) and 90 wt% (maximum value) after applying 1 V/cm during 24 h at a pH 9.

From this study, it is concluded that or abrasives from a mixture of solid powders of 30 wt% Si and 70 wt% abrasives (SiC or Al_2O_3) by using electrophoresis and gravitational settling. This study concluded that considering the use of Al_2O_3 as abrasives instead of SiC for cutting Si ingot might be advantageous in the view of its larger density and higher isoelectric point (IEP) than SiC. Moreover, the recovery of material with high Si content can provide for the Si source for solar cell production by a subsequent high-temperature treatment and dimensional solidification of solar-grade silicon; and, the abrasives can be reused in the sawing process.

Another investigation, reported by Wu and Chen (2009) [7], separated Si and SiC from wire saw slurry. A cell with pair of platinized titanium electrodes was used for the separation of different particles and it was evaluated in a buffer solution by gravity combined with electrical fields. Buffer solutions with pHs of 2, 7 and 8 were prepared using H_3PO_4 and NH_3. The solutions collected at different positions were measured using static light scattering (Beckman, Coulter LS230) and a Horiba carbon/sulfur analyzer. The Zeta potential analyzer (Zetasizer 3000; Malvern) was used to determine the surface charges of these particles at various pHs. The PSD and SiC content at each position was then determined to investigate separation efficiency (Fig. 4).

Near the cell outlet, only 7.15 wt% SiC remained in the mixture achieving the highest efficiency of separation, the original mixture had around 75.3 wt% SiC. It is worth mentioning that separation of Si from wiresaw slurries by centrifugation is often inadequate for complete metal fragments removal. Wu and Chen's study pretreated the slurries to remove metal impurities. This pretreatment included the approaches of electro kinetics and acid dissolution instead of centrifugation. After metals were removed by either method, the solid components were 50–55 wt% of the original slurries.

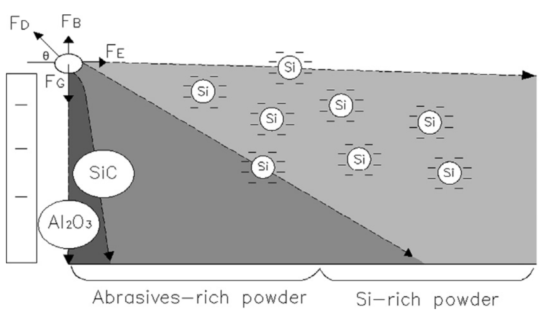


Fig. 4. Schematic diagram of particles moving in an electrical field.

This study supported the recycling of silicon through the recovery of material with high Si content that can reduce the high cost of silicon feedstock for the production of solar cells.

3.2. Alloying process

Wang et al. (2012) [2] studied the removal of silicon carbide from kerf loss slurry waste by the Al–Si alloying process. A novel approach to remove silicon carbide from the slurry waste by solidification refining with Al addition was assessed.

They proposed that glycol solution and metal fragments were removed by acetone and nitric acid leaching, respectively, whereas powders containing 74 wt% Si and 26 wt% SiC were applied as the starting material, after which it was used for Al–Si alloying ingot preparation.

A sample with $1 \times 0.8 \times 0.6\ mm^3$ was extracted from the central part of the ingot, followed by polishing of the sample's bottom with 1 μm diamond paste. The surface and bottom of the sample are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), XRF and electron probe microanalysis (EPMA). According to their results and the characterization they presented, high purity silicon can be recovered from the Al–Si alloy.

The XRD patterns showed that the silicon carbide had been completely removed after the Al–Si alloying process and intermediate phase, Al_4C_3 was detected on the top surface of Al–Si ingot which is attributed to the formation of Al_4C_3 with hexagonal crystalline structure.

The Al/Si ratio was determined by EPMA. EPMA analysis showed a mixed layer with a thickness of approx. 200 μm. EDS analysis reported that the composition of the mixed layer was

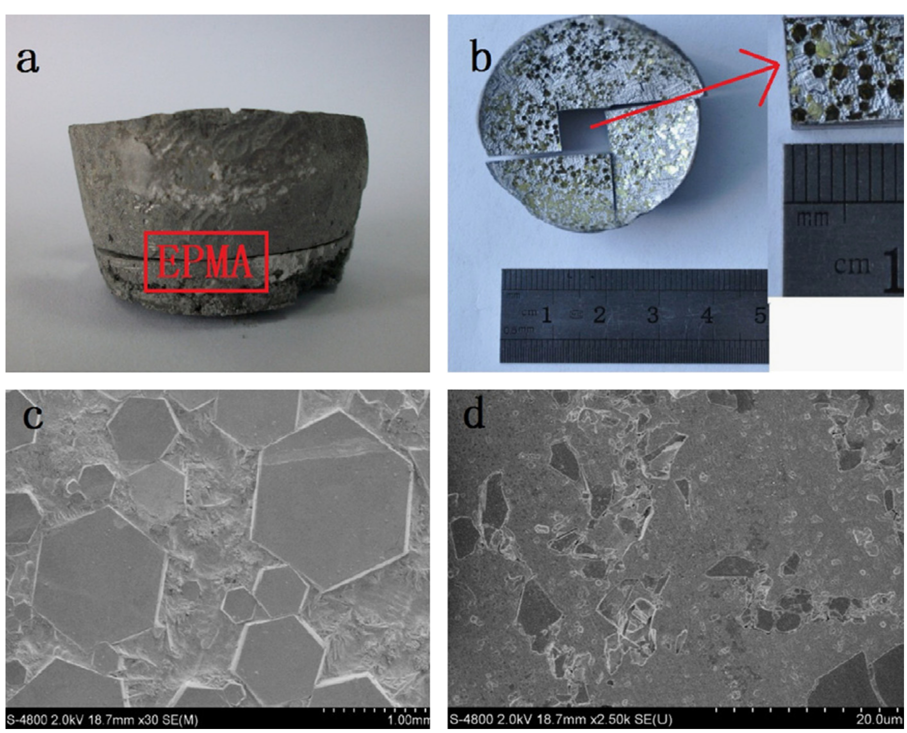


Fig. 5. Morphology of the Al–Si ingot: (a) Al–Si ingot, (b) top surface of Al–Si ingot, (c) SEM image of top surface of Al–Si ingot and (d) SEM image of bottom surface of Al–Si ingot.

Al–Si alloy and Al_2O_3 (Fig. 5). This result was also confirmed from the XRF analysis.

In addition to this finding, XRF analysis of the raw material and sample has clearly demonstrated that the C element was completely removed after the Al–Si alloying process. However, due to the formation of Al_4C_3, the C element could be detected on the top surface of the ingot but not after the polishing treatment in which it disappeared.

Authors concluded that Al–Si alloying process is a simple method to recycle the kerf loss slurry and to obtain high purity Si from Al–Si alloy ingot applying electrolysis or acid leaching.

3.3. Phase-transfer separation method

Lin and Tai (2010) [8] studied the recovery of silicon powder from kerfs loss slurry produced in the silicon wafer slicing process. They applied the phase-transfer separation method carrying out two stages for Si and SiC particles recovery from the powder mixture which was the starting material of the separation process after washing the kerfs loss slurry with acetone and nitric acid to remove the glycol and metal fragments, respectively. Due to the acid washing, the surface of the Si sample became more hydrophilic and the SiC particles remained hydrophobic, as determined by the contact-angle measurement.

In the first stage, the powder mixture was dispersed into oil that was heavier than water. Then, oil with a density lower than water was added into it. After a thorough stirring, the particles with hydrophobic surface moved into the heavier oil phase, mainly larger SiC particles, and the hydrophilic particles (Si) and most of the remaining submicron SiC remained in the water phase. Following the dispersion step (second-stage of separation), two liquid phases were easily separated after settling, and the preferred product was recovered.

The recovery process included the effects of several operating variables, such as: pH value of water phase; oil/water volume ratio; solid concentration; and, the purity and recovery of the Si product at specific working conditions. As a result, the highest overall recovery obtained was 71.1% and the highest Si purity achieved was 99.1 wt%.

3.4. Centrifugation

Lin et al., (2010) [8] demonstrated the potential feasibility of recovering silicon powder from kerf loss slurry waste applying the centrifugation process to decrease silicon shortage which is an issue of concern for the fast growing PV industry.

The experiment investigated wire-saw slurry compounded of silicon kerfs, silicon carbide abrasives, iron fragments, and glycol solution.

As first step for this experiment, a sample of 20 g was placed in a centrifuge tube, then 15 g of acetone was added and the tube content was mixed. Centrifugation and decanting were the methods used for the removal of the glycol solution in the slurry together with the acetone. When dried, the powder was weighed. After that, a 30 wt% nitric acid solution with a measured weigh of 55 g dissolved the metal fragments in the powder. Later, the reacted acid solution was removed by using centrifugation and, once more, the weight of the dried powder was recorded. Finally, in order to dissolved the silicon, two aqueous solutions of 200 ml containing 48 wt% HF and 30 wt% H_2O_2 were added dropwise to the watery slurry of the dried powder. Deionized water was used to wash the remaining SiC powder being then able to collect it by centrifugation. After drying, the weight of SiC was recorded in the data so that the composition of the slurry could be calculated.

The recovery process for Si powder consists mainly of four steps: (i) acetone washing, (ii) acid washing, (iii) centrifugation, and (iv) HF washing.

- Acetone washing: to remove ethylene glycol;
- Acid washing: to dissolve metal fragments;
- Centrifugation: to separate SiC and Si particles; and,
- HF washing: to remove boron and calcium coming from the glass fragments generated by the sawing.

A centrifuge with a rotating radius was applied for the separation of Si and SiC particles. As the specific gravity of the heavy-liquid fell between that of Si and SiC, both particles were acted in a counter-direction and separated. The authors claimed that the upper layer cake should be silicon and noticed that smaller particles of SiC were easily trapped in the cake (Fig. 5). The separated silicon cake visible on the top was scooped out and washed with a solution of 95 wt% acetone so that the heavy-liquid was removed. A solution of 10 wt% HF to remove the boron and calcium was also applied as washing. Finally, deionized water washed the acid content and the moist powder was dried by vacuum being ready for analysis. (Fig. 6).

The variables studied in the centrifugation step were: (i) solid volume fraction, (ii) heavy-liquid density, (iii) number of centrifugation step and (iv) centrifugation time and (v) agitation time.

By settling the solid volume concentration at 6.5%, the heavy-liquid density at 2.35 g cm^{-3}, the agitation time at 60 min, and the centrifugation time at 60 min, a product with Si purity of 90.8 wt% and a yield of 74.1% was obtained. The recovered Si can become further solar-grade silicon if processed properly.

The same research group (Wang et al., 2009) [10] carried out a research work on the recovery of high quality silicon from kerf slurry waste combining chemical treatment, heavy-fluid high-gravity centrifugation, high-temperature treatment, and, directional solidification (Fig. 7). The raw material was obtained from the Chu-Nan's factory of the Sino-American Silicon (SAS) products Inc., Taiwan. It should be noticed that this latter is a residue derived during wafer slicing from p-type Czochralski grown single crystalline Si ingots with a resistivity in the range of 0.5–5 Ω cm which is different from polycrystalline silicon manufacturing process.

They reported a promising approach to recycle kerf loss silicon from cutting slurry waste for solar cell applications. Silicon carbide (SiC) and metal impurities were successfully removed by chemical/physical processing from the slurry waste to recover solar grade silicon. Metal impurities were successfully removed to an acceptable level for solar cell applications. The effects of centrifugation using heavy fluids were similar to those related in the previous section. In addition to the first investigation, high-temperature treatment was performed aiming to remove very small particle size of SiC remaining in the raw material. This was done in order to manufacture ingots from the recycled silicon and to compare it with the original sawing silicon ingots [10].

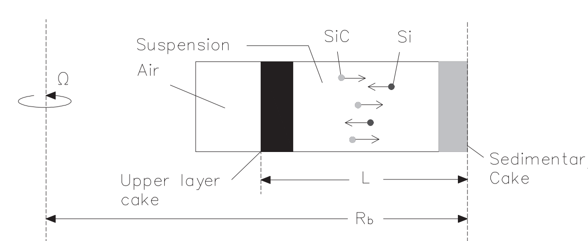


Fig. 6. Material distribution in the centrifuge tube after centrifugation where: Rb is the radius from the rotor center to the rotating tube bottom; L is the suspension height and Ω is the rotational speed of centrifuge.

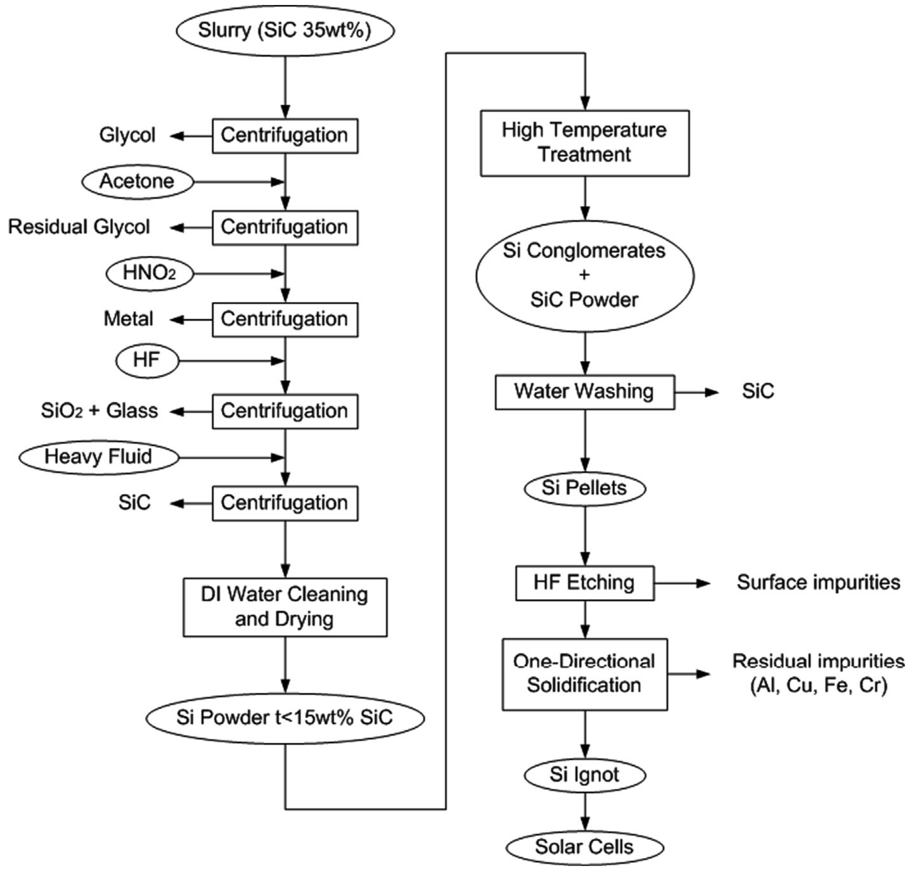


Fig. 7. Schematic flow diagram of the recycling process for silicon recovery.

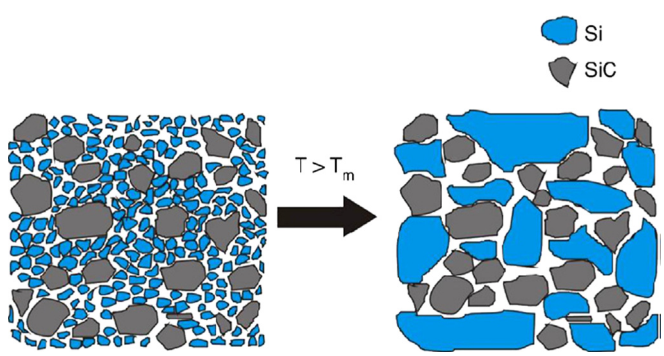


Fig. 8. Schematic illustration of silicon conglomeration during high-temperature Treatment.

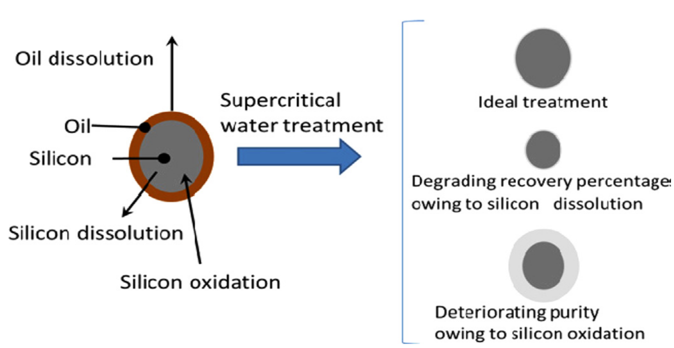


Fig. 9. Schematic diagram: Supercritical water elutriation of silicon sludge.

In the HT treatment, Si/SiC powder was first palletized. The pellet was placed in a silicon nitride coated quartz crucible with an inner diameter of 46 mm and was subjected to the HT treatment for several hours at about 1470 °C in an argon atmosphere and using an induction furnace. As a result of the difference in the melting points of the constituents, Si started oozing out of the material in the form of clusters during HT treatment. The formation of clusters is schematically shown in Fig. 8. Once the cluster formation was over, the material was cooled down. The silicon clusters and SiC were easily separated by simple water cleaning due to the fact that Si clusters were non-adherent to the SiC particles. Moreover, most of the other impurities were segregated towards the surface of the Si conglomerates during the cooling down stage which where washed away from this conglomerate skin using hydrofluoric acid. The silicon was further cleaned by DI water and used for crystal growth by directional solidification applying a silicon nitride-coated quartz crucible [11].

The obtained Ingots from the recycled silicon were grown by directional solidification. The average resistivity and minority carrier lifetime of the grown crystals were found to be about 1.02 μs and 0.7 Ω cm, respectively, which were close to the original sawing silicon ingots. Solar cells using multi-crystalline wafers of recovered silicon were fabricated with an energy conversion efficiency of 12.6% close to that from the high-purity silicon [10].

3.5. Supercritical water

In a recent investigation, Yoko and Oshima (2013) [5] suggested a new methodology for removing oil from silicon by supercritical water elutriation in a semi-batch reactor system. In this investigation,

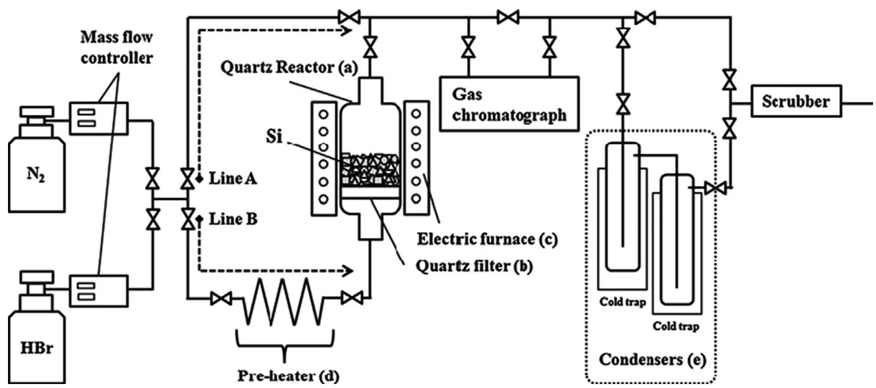


Fig. 10. Schematic representation of the experimental set-up: Hydrobromination of silicon.

Table 1
Chemical analysis of impurity concentration before and after hydrobromination reaction of MG-Si and kerf loss silicon [9].

Element concentration (ppmw)				
	MG-Si(i)		Kerf loss silicon(ii)	
	Before reaction	After reaction	Before reaction	After reaction
Al	2376.4	280.77	5859.35	12.68
B	22.22	18.08	< 2.64	< 2.64
Ca	587.59	21.45	< 0.09	< 0.09
Cr	13.76	2.13	< 0.29	< 0.29
Fe	2638.02	< 0.32	153.22	19.44
K	61.58	69.43	517.3	64.44
Na	67.77	77.17	55.83	43.93
Ni	15.34	< 0.64	166.46	0.65
P	186.03	73.55	74.79	73.71
Ti	202.03	130.14	47.75	10.40
Zn	22.13	22.69	3.24	3.66

N_2 30 mL/min: reaction temperature, 400 °C (i) and 420 °C (ii).

Table 2
Chemical analysis of impurity concentration before and after hydrobromination reaction of reagent grade silicon RG-Si; metallurgical grade silicon MG-Si and kerf loss silicon KL-Si [4].

Contents of metal elements in Si samples and the hydrolyzed products Element concentration (ppmw)									
	RG-Si			Mg-Si			KL-Si		
	Before reaction	After reaction		Before reaction	After reaction		Before reaction	After reaction	
		Si	Si/SiC		Si	SiC		Si	Si/SiC
Al	876	55	35	2645	16		6368	49	60
Cu	6	5	5	2	2		6	3	1
Fe	3277	8	8	3179	11		214	11	8
Ni	3	ND	ND	1	ND		256	ND	ND
P	33	6	8	21	ND		4	ND	ND

the interest was the recovering of high-purity silicon from the silicon sludge which is the waste discharged from the silicon ingot cutting process consisting of a mixture of cutting oil, cooling water, and silicon particles. The Schematic diagram illustrating the supercritical water elutriation of silicon sludge is shown in Fig. 9.

Yoko and Oshima concluded that the recovery of high-purity silicon applying the aforementioned method is possible. The oil contained in silicon sludge was completely removed in about 30 min by the means of supercritical water elutriation at 400 or 500 °C and 25 MPa. Only 70% at 400 °C was the recovery percentage of silicon due to silicon dissolution. Nevertheless, a greater result with a value of 95% was obtained at a higher temperature of 500 °C which was achieved because of silicon dissolution suppression owing to the low ion product of water at higher temperatures. This difference in silicon recovery was explained by the fact that the rate of silicon dissolution is accelerated as the temperature is increased in this range. In contrast, at 400–500 °C, the amount of dissolved silicon decreased with increasing temperature. As a final finding, the recovered silicon at 500 °C was approximately 99.2% pure.

In addition to silicon recovery, the authors also studied quantitatively the oxidation and dissolution of silicon in supercritical water in terms of their effect on the recovery percentage and purity. During the experiment, they used a silicon substrate to observe the silicon oxide growth and concluded that the decrease in the purity due to silicon oxidation was negligible under the studied conditions which supported the high-purity silicon percentage recovered from the silicon sludge.

3.6. Hydrobromination

Tomono et al., (2012) [3] study, two types of silicon, metallurgical-grade silicon and kerf loss silicon were investigated in a flow reactor system.

Prior to hydrobromination reaction, the kerf loss silicon was pretreated as follows: A wire-saw slurry sample of 20 g was placed in a centrifuge tube, then, 20 g acetone was added and mixed. The solution obtained was centrifuged and decanted to remove glycol, acetone and others two times. After drying at 100 °C under vacuum over 24 h, the dried Si powder sample was subjected to the reaction with HBr.

Fig. 10 shows a schematic representation of the experimental set-up used for the hydrobromination of silicon.

The process consisted in the addition of HBr gas in the quartz reactor for hydrobromination of silicon with a temperature range between 370 and 450 °C. The exhaust gas was passed through double condensers cooled at −40 and −30 °C. The condensed products were hydrolyzed into silicon dioxide (SiO_2) and HBr by exposing them slowly with water vapor in air. Then, the resulting SiO_2 products were subjected to ICP-AES characterization.

Table 1 shows the concentrations of impurities before and after the hydrobromination reaction of MG-Si and kerf loss silicon. The typical impurities contained within the kerf loss silicon are aluminum and nickel due to the worn down metals (nickel and iron) from the coating agent and steel wire of a fixed abrasive steel saw wire [9]. The source of aluminum was recognized to be the aluminum mounting stage during wafer slicing. Kerf loss silicon is known to contain lower metallic impurities than MG-Si, with the exception for aluminum and nickel. Phosphate from industrial water may contaminate the waste sample and thus reveal a

relatively high concentration of phosphorous before reaction, compared to that in the original PV-grade silicon.

On the other hand, Table 2 shows the concentration of impurities before and after the hydrobromination reaction with and without SiC abrasives as a purification of kerf loss waste (Tomono et al., 2013) [4].

In this study, three types of silicon were investigated, reagent grade silicon RG-Si; metallurgical grade silicon MG-Si and kerf loss silicon KL-Si. The same process as described above was used under a temperature of 400 °C.

Metal impurities such as Al, Fe, and Ni in the starting materials were dramatically decreased in the products.

Addition of SiC resulted in no significant increase in impurities. Rather, it accelerated the reaction kinetics in the temperature region of 350–400 °C. Probably, this was a result of better heat transfer owing to its high thermal diffusivity. Consequently, it was concluded that the bromination process enables the extraction of pure silicon from the sawing waste without pre-removing of SiC.

4. Conclusions

A variety of methods for the efficient recovery and/or recycling of high purity silicon from the kerf loss slurry waste have been reviewed in the present work.

The crystalline silicon technology domaining the PV market aims for the reduction in cost per watt which results challenging this industry. Cost reduction in this technology is largely driven by the know-how accumulated from many years from the industrial manufacture and the system operating timeline, allowing robust extrapolations to future costs.

In order to ensure the continuous growth of the crystalline-silicon solar cells industry in the next century, extensive research and development of innovative and feasible approaches for producing low-cost polysilicon feedstock through solar grade Si separation processes are a need in the near future, representing promising savings for the solar cell application.

References

[1] A Strategic Research Agenda for Photovoltaic Solar Energy Technology EDITION 2 2011. ⟨http://www.eupvplatform.org/publications/strategic-researchagenda-implementation-plan.html⟩.

[2] Wang HY, Tan Y, Li JY, Li YQ, Dong W. Removal of silicon carbide from kerf loss slurry by Al–Si alloying process. Sep Purif Technol 2012;89:91–3.

[3] Tomono K, Okamura Y, Furuya H, Satoh M, Miyamoto S, Komatsu R, et al. Selective hydrobromination of metallurgical-grade silicon in a flow reactor system. J Mater Sci 2012;47:3227–32.

[4] Tomono K, Furuya H, Miyamoto S, Okamura Y, Sumimoto M, Sakata Y, et al. Investigations on hydrobromination of silicon in the presence of silicon carbide abrasives as a purification route of kerf loss waste. Sep Purif Technol 2013;103:109–13.

[5] Yoko A, Oshima Y. Recovery of silicon from silicon sludge using supercritical water. J Supercritical Fluids 2013;75:1–5.

[6] Tsai TH. Silicon sawing waste treatment by electrophoresis and gravitational settling. J Hazard Mater 2011;189:526–30.

[7] Wu YF, Chen YM. Separation of silicon and silicon carbide using an electrical field. Sep Purif Technol 2009;68:70–4.

[8] Lin YC, Tai CY. Recovery of silicon powder from kerfs loss slurry using phase-transfer separation method. Sep Purif Technol 2010;74:170–7.

[9] Lin YC, Wang TY, Lan CW, Tai CY. Recovery of silicon powder from kerf loss slurry by centrifugation. Powder Technol 2010;200:216–23.

[10] Wang TY, Lin YC, Tai CY, Fei CC, Tseng MY, Lan CW. Recovery of silicon from kerf loss slurry waste for photovoltaic applications. Prog Photovolt: Res Appl 2009;17:155–63.

[11] Wang TY, Lin YC, Tai CY, Sivakumar R, Rai DK, Lan CW. A novel approach for recycling of kerf loss silicon from cutting slurry waste for solar cell applications. J Crystal Growth 2008;310:3403–6.

[12] Peng J, Lu L, Yang H. Review on life cycle assessment of energy payback and greenhouse gas emission of solar photovoltaic systems. Renew Sustain Energy Rev 2013;19:255–74.

[13] Ferber RR, Costogue EN, Pellin R. Polycrystalline silicon availability for photovoltaic and semiconductor industries. Int J Solar Energy 1982;1:105–24.

[14] Del Coso G, Del Canizo C, Sinke WC. The impact of silicon feedstock on the PV module cost. Solar Energy Mater Solar Cells 2010;94:345–9.

[15] Yamane H, Morito H, Uchikoshi M. Formation of Si grains from a NaSi melt prepared by reaction of SiO_2 and Na. J Cryst Growth 2013;377:66–71.

[16] Hardin CW, Qu J, Shih AJ. Fixed abrasive diamond wire saw slicing of single-crystal silicon carbide wafers. Mater Manufactur Process 2004;19:355–67.

[17] Kim H, Kim D, Kim C, Jeong H. Multi-wire sawing of sapphire crystals with reciprocating motion of electroplated diamond wires. CIRP Annals — Manufactur Technol 2013;62:335–8.

[18] Yu X, Wang P, Li X, Yang D. Thin Czochralski silicon solar cells based on diamond wire sawing technology. Solar Energy Mater Solar Cells 2012;98:337–42.

[19] Dongre G, Singh R, Joshi SS. Response surface analysis of slicing of silicon ingots with focus on photovoltaic application. Machining Sci Technol 2012;16:624–52.

[20] Drouiche N, Naceur MW, Boutoumi H, Aitmessaoudene N, Henniche R, Ouslimane T. Assessment of the recovery of photovoltaic cells cutting fluid by chemical pretreatment and ultrafiltration. Desal Water Treat 2013;51:713–6.

[21] Radeker W St. Cunningham SW. A hierarchy of slurry reprocessing options. TMS Conference Papers, Seattle, Washington: February 14–18, 2010.

[22] Graf RF. Modern Dictionary of Electronics (Seventh Edition), 1999; P. 759–812.

[23] Petter K, Q-Cells SE. Materialaspekte multikristalliner Solarzellen aus umg-Si-Feedstock. FAHL Academia, Oppurg, 29. September 2009.

[24] Drouiche N, Djouadi-Belkada F, Ouslimane T, Kefaifi A, Fathi J, Ahmetovic E. Photovoltaic solar cells industry wastewater treatment. Desal Water Treat 2013;51:5965–73.